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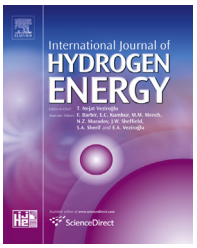

Performance and stability of single and 6-cell stack passive direct methanol fuel cell (DMFC) for long-term operation

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ABSTRACT

A passive, air-breathing, 6-cell direct methanol fuel cell (DMFC) stack is designed, fabricated and tested based on the performance of a passive single-cell DMFC. A large methanol reservoir in a hexagonal shape is considered in designing the stack in order to increase the DMFC operation time without any interruption, i.e., to refill the methanol solution. Hence, the ratio of methanol solution volume in the reservoir for the single cell, i.e., 8 ml, and hexagonal stack, i.e., 240 ml, is 1:30. The power output of 500 mW is achieved at 1.5 V using a 5 M methanol solution at room temperature. With a large volume of methanol, i.e., 240 ml of 5 M methanol in the hexagonal stack, it can be operated continuously at 1.5 V for more than 40 h, whereas for a small volume, i.e., 8 ml in a single cell, the operation can reach only 3 h–4 h with a similar reduction of 25% from the initial power output. Moreover, the DMFC stack is used for long-term operation more than 3000 h, and the morphology of MEA is analyzed.

Introduction

Recently, there has been considerable interest in the use of direct methanol fuel cells (DMFCs) to replace conventional batteries for powering portable electronic devices [1–4]. Over the past decade, in many published reports, much effort by researchers has been devoted toward the development of new electro catalysts [5–7] and electrolyte membranes [8,9] to overcome the persistent technical barriers of DMFCs. These barriers include the slow kinetics of methanol oxidation and oxygen reduction reactions, cathode catalyst poisoning, and high methanol crossover (MCO) through the electrolyte membrane. Methanol crossover occurs when the methanol feed to the anode compartment diffuses through the separating membrane into the cathode compartment, which is a significant problem that limits the performance of DMFCs. However, most of this research has focused only on the behavior of the

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DMFC performance in a half-cell or single-cell configuration. Furthermore, compared with single cells, the development of a fuel cell stack system is more challenging because of power fluctuations that occur during the integration of single cells into the stack [10]. In order to have high efficiency of the system, the crucial design parameter is to develop the DMFC stack, i.e., including cell components such as the membrane electrode assembly (MEA), to produce high methanol utilization efficiency with sufficient power to operate the system [11].

Based on a literature review, several studies on the development of DMFC stacks are reported with different system designs and materials used. For instance, Cao et al. fabricated two mono-polar 6-cell DMFC stacks with two different anode flow fields on silicon substrates [12]. Each single cell had an active area of 1.4×1.4 cm^2. The volume and weight of the stack were only 5.3 cm^3 and 10.7 g, respectively. Based on their experiment, the results showed that the stack with double serpentine-type flow fields could generate better performance, with maximum output power reaching 151 mW at a voltage of 1.5 V [12]. Moreover, Guo et al. developed a 4-cell DMFC stack on a printed circuit board (PCB) with a total active area of 76.6 cm^2 and obtained a maximum power output of 320 mW at 0.35 A using a 50 cm^3 methanol solution [13]. In addition, Zhu et al. developed a twin stack containing planar 8-cell DMFCs with stack dimensions of 13 cm $\times$ 2 cm $\times$ 10 cm. The stack, equipped with a fuel feed device, successfully powered a sensor node for 39 h while consuming 80 ml of 4 M methanol. A peak power density of 16.9 mW cm^{-2} was achieved, and the power output of 540 mW at 1.8 V was obtained [14].

In all of the above and other published [15,16] reports on the development of DMFC stacks, the stack performance and efficiency were dependent on the 1) Design of the stack, i.e., MEA properties such as catalyst loading; 2) Stack configuration, i.e., stack design and materials used; and 3) The operating parameters, i.e., methanol concentration, temperature, flowrate; and system operating mode, i.e., active, semi-passive or passive. For instance, Baglio et al. studied the effect of catalyst loading in the MEA and methanol concentration in their DMFC stack. They found that the maximum power was obtained at an ambient temperature with 4 mg cm^{-2} Pt loading (varied from 1.5 to 6.0 mg cm^{-2}) using 5 M methanol concentration (varied from 1 to 10 M) [17].

In the case of the stack configuration, most researchers have concentrated on a compact stack design that is lighter, is easier to handle and saves space. However, the compact stack design has drawbacks, such as limits on the methanol fuel volume in one-time operation for the passive system DMFC. This would affect the operation time of the DMFC stack because methanol acts as a reactant for the anode reaction and hence affects the time management in order to refill the methanol fuel. However, several papers reported and considered a large methanol reservoir or tank for the passive system DMFC stack [14,18]. For instance, Guo and Faghri developed a 1 W passive DMFC stack with a total active area of 72.0 cm^2. The stack could be filled with 500 g (approximately 500 ml) of 3 M methanol solution at a time, and a power output of 1.5 W was achieved at 2.4 V at room temperature. Moreover, the stack continuously ran at 33 mA cm^{-2} for 57 h and generated total electrical energy of 26.1 Wh [18].

Nevertheless, improving performance and long-term stability are key factors for the success of DMFCs in the market. Because different phenomena are involved in the current generation of DMFCs, i.e., charge transfer reaction, mass transport, adsorption processes, etc., the measured performance loss due to degradation of the MEA can be the result of various causes [19]. For instance, Cheng et al. revealed that there was significant performance degradation after 1002 h of operation. Increases in the catalyst particle size from both the anode and cathode catalysts were observed after the DMFC lifetime test. Changes in the microstructure, surface composition, interfacial structure of the MEA, and aging of Nafion® under the DMFC lifetime tests were also observed [20].

In this work, a passive system DMFC stack was designed, fabricated and evaluated based on the performance of a single-cell DMFC. A large fuel reservoir was considered in the stack design in order to increase the operation time of the DMFC stack. However, the geometric shape and size of the DMFC stack were different from those of Guo and Fagri's DMFC stack [18], i.e., hexagonal and rectangular geometric shapes and the approximate maximum methanol solution used 280 ml and 500 ml for this study and Guo and Fagri's work, respectively. A detailed explanation of the advantages of the hexagonal shape used in this study will be discussed in the experimental section. Moreover, the passive single cell and the stack of DMFCs were operated with dilute methanol solutions with concentrations varying from 2 to 6 M. The power output and stability performance of the stack were measured for long-term operation. The effects of the methanol concentrations and operation time will be discussed based on stack power, stability and degradation of stack performance.

Experimental

MEA fabrication for single cell and DMFC stack

Nafion 117 electrolyte membrane (DuPont™) was used as an electrolyte membrane. Platinum (Pt)/Ruthenium (Ru)-black (HiSPEC 6000, Alfa Aesar, USA) and Pt-black (HiSPEC 1000, Alfa Aesar, USA) were used as catalysts for the anode and cathode, respectively. Commercial carbon cloth (E-TEK, USA) was used as a backing layer with 2.0 mg cm^{-2} of carbon black loading with 5 wt% polytetrafluoroethylene (PTFE) serving as a diffusion layer at the anode and cathode. The catalyst inks were prepared by dispersing an appropriate amount of the catalyst in a solution of deionized water, isopropyl alcohol, and 5 wt% Nafion® solution (Wako Pure Chemical Industries, Ltd.). For the anode, Pt–Ru ink and Pt ink were coated on the diffusion layer for the anode and cathode, respectively. Catalyst loading on both the anode and cathode is 8.0 mg cm^{-2}. The MEAs with 4 cm^2 active areas were then fabricated by sandwiching the membrane between the anode and cathode and hot pressing them at 135 °C and 5 MPa for 3 min.

Passive DMFC stack design

In this study, a passive single cell and stack were operated to compare the performance of each unit. For the single cell of

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